BIOPETROL SYNTHESIZED FROM RUBBER SEED OIL THROUGH HETEROGENEOUS CATALYTIC CRACKING USING ZEOLITE CATALYST: EFFECT OF ACETONE IN SOLVENT EXTRACTION OF RUBBER SEED

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ABSTRACT

Today scenario imposes great importance on the alternative of fossil fuel. In line with that is the development of biofuel derived from biomass. Common feedstocks for such process nowadays are corn, soya oil, palm oil etc. However, the rubber seed oil (RSO) can be extracted from its kernel to be derived as biopetrol. This method is much favarouble as the high concentration of fatty acids in rubber seeds. Also, rubber seeds are abundant and easily available throughout Malaysia. It will also be a secondary income for rubber plantation workers via collecting rubber seeds and selling it. The objectives of this experiment are; to synthesize isooctane form rubber seed oil using Zeolite as catalyst, to study the effect of solvent (Acetone) in the extraction of fatty acids from rubber seeds, and to analyze isooctane concentration through gas chromatography. Rubber seeds' kernel are cleaned, shelled, ground, blended, and dried. Extraction of fatty acids from rubber seeds are done by Soxhlet extraction method using Acetone as extraction solvent. The efficiency of solvent is analyzed by using different mass ratio between the solvents and rubber seeds kernel starting from 1:2 to 1:5. Rotary evaporator was used to evaporate the solvent, leaving behind crude rubber seed oil. The catalytic cracking of the mixture of 25ml of RSO and 5g of Zeolite catalyst at 350^0C for 45 minutes is to boost up the rate of reaction of breaking the long chains of fatty acids. The final product is analyzed through Gas Chromatography. Then the results of chromatograms are compared with the standard isooctane calibration curve. Through the calibration curve using backward calculation, the yield of biopetrol is determined. From this experiment the actual Isooctane concentration is about 53% to 78%. The result shows higher than expected result because of the factor of random reaction in catalytic cracking, hydrocarbon isomerization, high quantity of fatty acids in rubber seed oil which have been converted to Isooctane, and the small volume of sample analysis. This research can be further improved by the use of Supercritical CO^2 in extraction process, filling of inert gases or nitrogen in catalytic cracking chamber, elimination of impurities and minimization of human errors.

ABSTRAK

Senario hari ini mengenakan amat penting pada alternatif bahan api fosil. Sejajar dengan itu adalah pembangunan biofuel yang diperolehi dari biomass. Bahan utama biasa untuk proses itu kini adalah jagung, minyak soya, minyak sawit dan sebagainya. Walau bagaimanapun, minyak getah benih (RSO) boleh diekstrak daripada isirongnya yang akan disintesis sebagai biopetrol. Kaedah ini adalah lebih digemari oleh hal kerana kepekatan asid lemak dalam biji getah yang tinggi. Juga, biji getah yang banyak dan mudah didapati di seluruh Malaysia. Ia juga akan menjadi pendapatan tambahan bagi pekerja-pekerja ladang getah melalui memungut benih getah dan menjualnya. Objektif eksperimen ini adalah untuk sintesis isooctane daripada minyak benih getah menggunakan zeolit sebagai pemangkin, untuk mengkaji kesan pelarut (aseton) dalam pengekstrakan asid lemak daripada benih getah, dan untuk menganalisis kepekatan isooctane melalui kromatografi gas. Isirong benih getah dibersihkan, dan dibiarkan kering semalaman. Untuk mengeluarkan asid lemak daripada benih getah, perlu dilakukan melalui kaedah pengekstrakan Soxhlet menggunakan aseton sebagai pengekstrakan pelarut. Kecekapan pelarut dianalisis dengan menggunakan nisbah jisim yang berbeza di antara pelarut dan getah kernel benih bermula 1:2 hingga1:5. Penyejat Rotary telah digunakan untuk menyejat pelarut, meninggalkan minyak benih getah mentah. Keretakan pemangkin dilakukan dengan campuran 25ml RSO dan 5g zeolit pemangkin pada suhu 350^{0}C selama 45 minit adalah untuk meningkatkan kadar tindak balas memecahkan rantaian panjang asid lemak. Produk akhir dianalisis melalui Kromatograpi gas. Kemudian keputusan kromatogram dibandingkan dengan keluk penentukuran isooctane standard. Melalui keluk penentukuran menggunakan pengiraan mundur, hasil kepekatan yang sebenar biopetrol ditentukan. Daripada eksperimen ini kepekatan Isooctane sebenar adalah kira-kira 53% kepada 78%. Hasilnya menunjukkan lebih tinggi daripada hasil yang dijangka kerana faktor reaksi rawak dalam retak sebagai pemangkin, pengisomeran hidrokarbon, kuantiti yang tinggi asid lemak dalam minyak biji getah yang telah ditukar kepada Isooctane, dan kelantangan kecil analisis sampel. Kajian ini boleh terus diperbaiki dengan penggunaan kaedah Supercritical CO_2 dalam proses pengekstrakan, mengisi gas lengai atau nitrogen di dalam kebuk pemangkin retak, penghapusan kekotoran, dan mengurangkan kesilapan manusia.

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LIST OF SYMBOLS

P	-	Pressure
m	-	Mass
ΔH	-	Enthalpy change of reaction
ΔS	-	Entropy change of reaction
ΔG	-	Energy change of reaction
T	-	Temperature
ρ	-	Density
μ	-	Viscosity of liquid (Pa.s)
h	-	Heat transfer coefficient
^{o}C	-	Degree Celsius
g	-	Gram
kg		Kilogram
K	-	Degree Kelvin
m	-	Meter
ml	-	Mililiter
L	-	Liter

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CHAPTER 1

INTRODUCTION

1.1 FUEL CONSUMPTION SCENARIO

The recent increases in crude oil prices have created unprecedented opportunities to displace petroleum-derived materials with biofuel. Biofuel, as an alternative fuel, has many merits and made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and nontoxic has low emission profiles and so it is environmentally beneficial. Apart from that, biofuel is a renewable fuel, helping to achieve the EU renewable energy target of 12% of total energy output to consist of renewable energy by 2010 (European Commission, 1997). Carbon dioxide produced by combustion of biofuel can be recycled by photosynthesis, thereby minimizes the impact of biofuel combustion on the greenhouse effect (KEorbitz, 1999; Agarwal and Das, 2001). Additionally biofuel has a relatively high flash point (150 °C), which makes it less volatile and safer to transport or handle than petroleum diesel (Krawczyk, 1996).In support of this increasing consumption there have been substantial increases in biofuel production in recent years, a trend that is expected to continue. The EIA (Energy Information Administration) foreseeable that demand for biofuel will be at least 6.5 million gallons in 2010 and 7.3 million gallons in 2020.

Based on biofuel's potential, demand could reach as much as 470 million gallons in 2010 and 630 million gallons in 2020. Now the major producer of biofuel in the world is Germany. It has produced 2539 million ton in 2009 whilst Malaysia nearly exported 76 million gallons of biofuel in 2009. This growth is the result of the construction of new production plants and the expansion of existing ones.

In early 80's a petroleum company from Brazil produced biopetrol with a mixture of 10% vegetable oil has been used in pre-combustion chamber engines to maintain total power without any alterations or adjustments to the engine. At that point, it was not practical to substitute 100% vegetable oil for diesel fuel, but a blend of 20% vegetable oil and 80% diesel fuel was successful. Some short-term experiments used up to a 50/50 ratio also provide good solution for well maintain engine (Fangrui et al., Ma, 1998). This advantage engine adaptability to vegetable oil mixture with diesel makes an enriching step towards the feasibility of engine combustion with nominal effects using biopetrol. The table below shows the comparison between biopetrol and fossil fuel.

Table 1.1: Comparison between Biopetrol and Fossil Fuel

Aspect	Biopetrol	Fossil fuel
Greenhouse gas emission and environmental issue	Sustainable and biodegradable Reduces greenhouse gas emission Environmental friendly	Not biodegradable Contains a large amount of sulphur and oxygen which causes incomplete combustion which emits greenhouse gases Pollutes the environment
Energy security	Renewable energy source which can be produced from biomass	Non- renewable energy source and its depleting at a faster rate
Engine performance	Increases engine life Improves performance and efficiency in the combustion process	Incomplete combustion in the engine Leads to accumulation of particles in engine

Economy	Creates new job opportunies Increases the agricultural demand for biomass for to produce biofuel	Extraction of fossil fuel has high production cost The reduce in fossil fuel sources causes fossil fuel price to raise

1.2 BACKGROUND OF STUDY

Alternative fuels for transportation are becoming increasingly important due to diminishing petroleum reserves and the environmental consequences of exhaust gases from petroleum-fuelled engines. The energy source, fossil fuel, upon which we have come to rely on so deeply, is in higher demand than ever before, which more energy is needed all around to fulfill this demand. Fossil fuel alone seems to be insufficient to cater to the needs of the global community. In light of this, it is in the world's best interest to devote a substantial amount of resources towards alternative forms of energy. Biofuel, as biodiesel in this context, is at the forefront of these alternatives due to its ability to fuel conventional gasoline engines with minimum or no modifications, as well as form blends with fossil diesel.

Since biodiesel synthesis and production has proven to be successful, so another kind of biofuel should be synthesized and developed. Biopetrol seems to be a better alternative where majority of vehicles used in Malaysia are petrol based vehicle. In most of the researches regarding biopetrol, the most preferable choice of synthesis is done by using fatty acid as starting material through heterogeneous catalytic cracking. In this study, the biopetrol is material fatty acid extracted from rubber seeds via Soxhlet method and the synthesis is carried out through catalytic cracking using Zeolite as catalyst.

Biopetrol is an environmentally friendly alternative liquid fuel. There has been renewed interest in the use of vegetable oils for making biopetrol due to its less polluting and renewable nature as against the conventional petroleum diesel fuel. The biggest difference between biofuels and petroleum feedstock is oxygen content. Biofuels have oxygen levels from 10% to 45% while petroleum has essentially none making the chemical properties of biofuels very different from petroleum.

1.3 PROBLEM STATEMENT

Due to the fact that the supply of fossil fuel is limited while energy demand continues rise, biofuel has been introduced as alternative renewable energy. The International Energy Outlook, an annual forecast by the U.S. Energy Information Administration forecast due to the driven by population and economic growth in developing countries, the world in 2035 would be more dependent on fossil fuels than ever, it finds. Countries overall would be consuming 49 percent more energy and spewing 43 percent more carbon dioxide into the atmosphere in 2035 than in 2007. To get rid from this problem, biofuel plays essential role in manner to reduce the emissions of carbon dioxide and reduce the consumption fossil fuel.

By using Zeolite as heterogeneous catalyst in this study would make the separation process easier and it also recyclable. The employment of homogeneous catalyst in the production of biodiesel has brought several disadvantages cause the catalyst can be dissolved in the methanol; the separation of catalyst from the product would be difficult. Thus, the manufacturing cost increases. Thus, the most feasible catalyst can be used in this study is Zeolite. This is due to the fact that aside from giving relatively high yield, it would monumentally reduce the length of processing time needed for production, and this would go well to supply the ever increasing rate of demand for alternative liquid fuel. With catalytic cracking, the biopetrol production industry in Malaysia would be able to cater to the needs of Malaysians at a faster rate, thereby eliminating the need for any dependence on foreign alternative fuel that may arise in the future. Malaysia would be able to deal with its own fuel crisis, at an optimal rate using its abundant feedstock resources.

1.4 RESEARCH OBJECTIVES

a) To extract fatty acid from rubber seeds kernel using Acetone as extraction solvent.

b) To synthesize isooctane from rubber seed oil through heterogeneous catalytic cracking using Zeolite as catalyst.

1.5 SCOPE OF STUDY

This study carried out by using rubber seed oil with Zeolite as base heterogeneous catalyst for the catalytic cracking reaction in lab scale reactor. In this study the following criteria have been given focus:

a) The extraction of fatty acid from rubber seeds using acetone as solvent via Soxhlet extraction.

b) Application of catalytic cracking method to crack the fatty acid complex molecule into smaller hydrocarbon molecules i.e. isooctane which is the most preferable.

c) Determination of the amount and concentration of isooctane using via an analysis using gas chromatography method.

1.6 RATIONALE & SIGNIFICANCE

The rationale and significance for this study are as below:

a) Biopetrol source which is rubber seed can be obtain in vast number because Malaysia has more than 1.7 million hector of rubber plantation.

b) Higher conversion of rubber seed oil would be achieved by catalytic cracking than thermal cracking by lowering the activation energy of the reaction.

c) Biopetrol is sulfur-free fuel and able reduce the emission of green emission gas thus making it environment friendly.

d) The cost of manufacturing will be reduced due to the simple process which is the purification process.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Finite petroleum reserves and the increasing demands for energy in industrial countries have created international unease. For example, the dependence of the United States on foreign petroleum both undermines its economic strength and threatens its national security. As highly populated countries such as China and India become more industrialized, they too might face similar problems. It is also clear that no country in the world is untouched by the negative environmental effects of petroleum extraction, refining, transportation and use. For these reasons, governments around the world are increasingly turning their attention to biofuels as an alternative source of energy.

Apart from the energy withdrawal with hydroelectricity and nuclear energy, the majority of the worlds energy needs are supplied through petrochemical sources, coal and natural gas. As these sources are finite and non renewable, at current usage rates will be consumed by the end of the coming century (Aksoy, 1990). In recent development, interest has arisen in the alternative sources for petroleum-based fuels which are with due concern of the depletion of world petroleum reserves and increased environmental concerns.

The use of vegetable oils as alternative fuel has been around since last century when the inventor of the diesel engine Rudolph Diesel first tested them, in his compression engine (Foglia, Jones,Haas, & Scott, 2000). Alternatively name for biofuel is oxygenated fuel, meaning that it emit low amount of carbon to the environment because it's contain higher hydrogen and oxygen than carbon (Armas *et al.*, 2008). Further supporting information, the sulphur contents of vegetable oils are close to zero and consequently, the environmental damage caused by sulphuric acid effects is reduced (Vicente *et al.*, 1998)

2.2 Fossil Fuel and Biofuel as Promising Alternative

Energy is an important factor of production in the global economy, and 90% of the commercially produced energy is from fossil fuels such as crude oil, coal, and gas, which are non-renewable in nature. Much of the energy supply in the world comes from geo-politically volatile economies. In order to enhance energy security, many countries, including the developed countries, have been emphasizing production and use of renewable energy sources such as biofuels, which is emerging as a growth industry in the current economic environment.(Thiam Leng,2006)

Nations like Brazil, the US, the European Union as well as many other countries around the world has given high priority for biofuels, due to concerns of oil dependence and interest in reducing CO2 emissions. All these regions have come up with significant subsidies for renewable energy production from agricultural sources. The impacts of these subsidies reach far beyond the borders of these economies. The global and sectoral implications of biofuel programs on agricultural markets and land use across the world seems much positive and gained significant response form the mass consumers. The very nature of biofuels production as a global economic activity affecting the pattern of energy demand and resource has motivated this study to initiate in the first place. When biofuels are mass produced and their usage is much preferred by consumers, the resulting impact of biofuel drives on output, prices, trade, land-use change, commodity price index, and job market.(Subash,Pramila 2006)

2.3 OCTANE NUMBER RATING FOR PETROL QUALITY

The quality of a fuel is measured with its 'octane number'. A good quality fuel has a good octane number. Octane number measures whether petrol is likely to cause knock in an engine. Knocking is caused by self-ignition in the engine's cylinders, which happens when the petrol/air-vapour mixture in the cylinder ignites before the plug sparks. This premature ignition pushes against the crankshaft instead of being with it, and produces a knocking or pinging sound. Knocking causes the engine to overheat and lose power, and it can damage the engine in the long run. In a properly functioning engine, the charge burns with the flame front progressing smoothly from the ignition point across the combustion chamber. Sometimes, at high compression ratios, depending on the composition and quality of the fuel, some of the charge may spontaneously ignite ahead of the flame front and starts to burn in an uncontrolled pattern. This will result in intense high frequency pressure waves followed by sharp sound which is actually caused by the premature combustion. (Reza Sadeghbeigi, 2000).

Octane rating crucial cause it reflects the quality, purity, refinement, efficiency and heat bearing capacity of petrol. It plays a role where it measures the ability of a fuel to resist knocking when ignited in a mixture with air in the cylinder of an internal combustion engine. As set by the petroleum industry, the octane number is determined by comparing, under standard conditions, the knock intensity of the fuel with that of blends of two reference fuels; isooctane which resists knocking and heptanes which knocks readily. In practical wise, the octane number is the percentage by volume of the isooctane in the fuel mixture of isooctane-heptane that similar to the fuel being tested in a standard engine. Normally, high Octane fuels are expensive because of high levels of refinement.(Agustin et al,2008)

The significant amount of isooctane in the fuel plays a defining role in choosing a reliable and engine safe which in turn provides the smoothness of ride and longevity of engine. Isooctane or in the standard form 2,2,4-trimethylpentane, is an octane monomer which defines the octane rating. This organic compound is highly branched that burns well with very little or negligible knock. By comparison, heptane is a straight, unbranched molecule with an octane rating of zero due to its high knocking properties.

In this case of study, biopetrol contains isooctane as its main constituent which gives it the characteristic to prevent knocking in the internal combustion engines. Meanwhile, the high concentration of oxygen in the biopetrol allows the engine to have much lower temperature combustion as well as reducing the emission of greenhouse gases such as carbon monoxide, and nitrogen oxides.

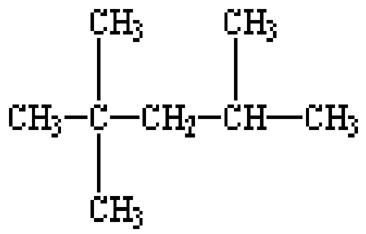

Figure 2.1: Chemical structure of Isooctane

Table 2.1: Physical & Chemical properties of Isooctane

Synonyms	Isobutyltrimethylpentane, 2,2,4-Trimethylpentane
Appearance	colorless liquid
Molecular formula	C_8H_{18} or $CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$
Molecular weight	114.22 g/mol
Melting point ^0C	-107.38°C (166K, -161^{0}F)
Boiling point ^0C	99.3°C (372K, 211^{0}F)
Density	688 kg/ m^3
Specific gravity	0.692
Solubility in water	Immiscible
Auto ignition temperature:	396°C

Source: Safety Data for Isooctane,2005

2.4 INNOVATION OF BIODIESEL

Fossil fuel alone seems to be insufficient to cater to the needs of the global community. In light of this, it is in the world's best interest to devote a substantial amount of resources towards alternative forms of energy. Biofuel, as biodiesel in this context, is at the forefront of these alternatives due to its ability to fuel conventional diesel engines with minimum or no modifications, as well as form blends with fossil diesel.

Biodiesel is defined as fatty acid methyl esters prepared from any kind of feedstock including vegetable oils, animal fats, single cell oils, and waste material. Fatty acid ethyl esters can also be defined as and used to produce biodiesel. However, due to the relatively high price of ethanol compared to methanol, the use of ethyl esters has not so far been established. The preparation of fatty acid methyl esters can be achieved by a process called transesterification, which is the exchange of alcohol or acid moiety of an ester. (A.S.Ramadhas,2005)

Alcoholysis is the transesterification of an ester with an alcohol, in which methanolysis is the term used in the case of methanol. The reaction requires a catalyst, usually a strong base, such as sodium or potassium hydroxide, and produces new chemical compounds called methyl esters. It is these esters that have come to be known as biodiesel. Because its primary feedstock is a vegetable oil or animal fat, biodiesel is generally considered to be renewable. Since the carbon in the oil or fat originated mostly from carbon dioxide in the air, biodiesel is considered to contribute much less to global warming than fossil fuels. Diesel engines operated on biodiesel have lower emissions of carbon monoxide, unburned hydrocarbons, particulate matter, and air toxics than when operated on petroleum-based diesel fuel.

All feedstocks that contain fatty acids or glycerol can be used for biodiesel production including rubber seed oil, jatropha *curcas* oil, and papaya oil. In European countries, rapeseed oil is used due to its widespread availability. Soybean oil is used in the Unites States of America, while palm oil is used widely in tropical regions such as Malaysia. The use of methyl esters as fuel requires a low proportion of saturated fatty acids in order to make the fuel function at low temperatures. In colder climates, rapeseed oil and olive oil have proven to be one of the best options. The usage of palm oil is ideal in Malaysia due its abundant availability as well as its suitability in warm climates. Palm oil can also be used as blends with other types of oil. Feedstock chosen is also influenced by national and international specifications of biodiesel that need to be fulfilled.(O.E.Ikwuagwu,2000)

2.5 BIOPETROL FROM FATTY ACIDS IN RUBBER SEEDS

Christopher Columbus is who the founder of rubber in tropical South America around 1500. Hevea brasiliensis, the common variety of rubber tree produces 99% of world's natural rubber. The seeds contain an oily endosperm. Generally, 37% by weight of the seed is only shell and the rest is kernel. The oil content of air dried is 47%.

Table 2.2: Fatty Acid Compositions in Rubber Seed Oil

Fatty acid composition (%)	Rubber seed oil
Palmitic acid	10.2
stearic	8.7
Oleic	24.6
Linoleic	39.6
Linolenic	13.2

Source: et al Shankaransh Srivastava, 2000

Fatty acid is a long unbranched aliphatic tail (chain) carboxylic acid, which is either saturated or unsaturated. Fatty acids can be saturated (acetic, butyric, palmitic acids), monosaturated (oleic acid), or polysaturated (linoleic, linolenic, arachidonic acids). Triglycerides from various vegetable oils give through transesterification a mixture of fatty acid esters which is now used increasingly as a substitute of diesel fuel and is named bio-diesel. Natural fatty acids are aliphatic monocarboxylic acids derived from, or contained in esterified form in an animal or vegetable fat, oil or wax. Natural fatty acids commonly have a chain of four to 28 carbons (usually unbranched and even numbered), which may be saturated or unsaturated (Aigbodion A.I. and C.K.S., Pillai, 2000).

Figure 2.2: Fatty acids

Shortly, the production of bio-petrol from fatty acids obtained from rubber seeds provides energy security in terms of domestic targets, supply reliability, reducing the dependability of fossil fuels, domestic distribution, ready availability and renewability. Besides that, the bio-petrol has proven its advantages over the other traditional fossil fuels by its multi characteristics. There is no sulphur molecule in its molecular structure and it is derived from biomass and thus, brings about the reduction of greenhouse gasses emission. Also, it is biodegradable and non-toxic, therefore it possesses the potential of being environmental friendly. It has the potential to enhance the performance, efficiency and life of engines as it contains isooctane that helps to prevent knocking. Despite that, the production of bio-petrol using rubber seeds will help to generate new job opportunities and new businesses to alleviate property that leads to a better, more stable economy in the country. The production of bio-petrol from rubber seed oil also will not lead to the detriment of food supply because rubber seeds are non-food crops. It has lower impact on marine environment as the water pollution can be reduced by using bio-petrol in the boat engines since there will be more efficient burning of the fuel mixture, less carbon accumulation and particulate emissions. Faster starting and smoother operation of engines by using bio-petrol could reduce the discharge of unburned fuel. Finally, any accidental discharges of small amount of bio-petrol have